Electronic Supplementary Material (ESI) for Dalton Transactions


# Electronic Supplementary Information

# Zeolitic imidazolate framework-71 nanocrystals and a novel SOD-type polymorph: Solution mediated phase transformations, phase selection *via* coordination modulation and density functional theory derived energy landscape

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## Contents

## 1. Synthesis and characterisation of NC-1

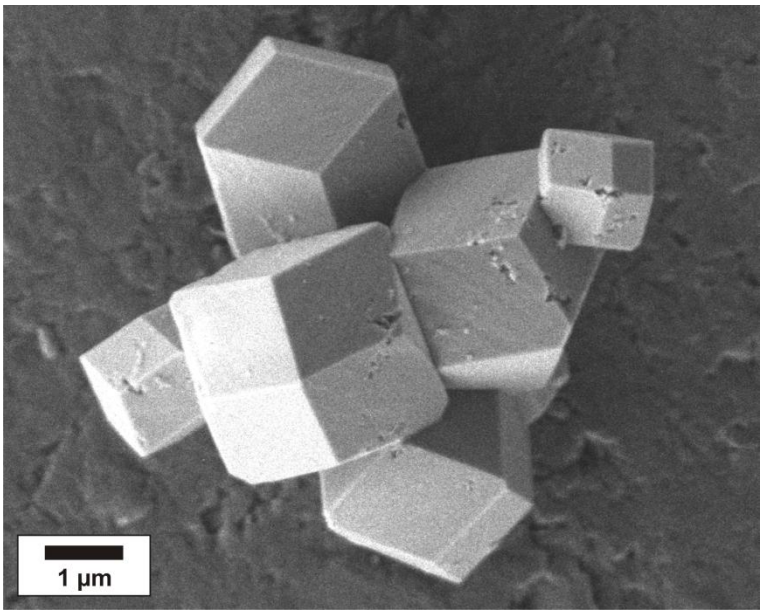


**Fig. S1** SEM image showing MC-**1** with rhombic dodecahedral shape obtained from solutions of composition $Zn(NO_3)_2 \cdot 6H_2O$/Hdcim/MeOH = 1 : 4 : 1000 after keeping at room temperature for 1 h without stirring.

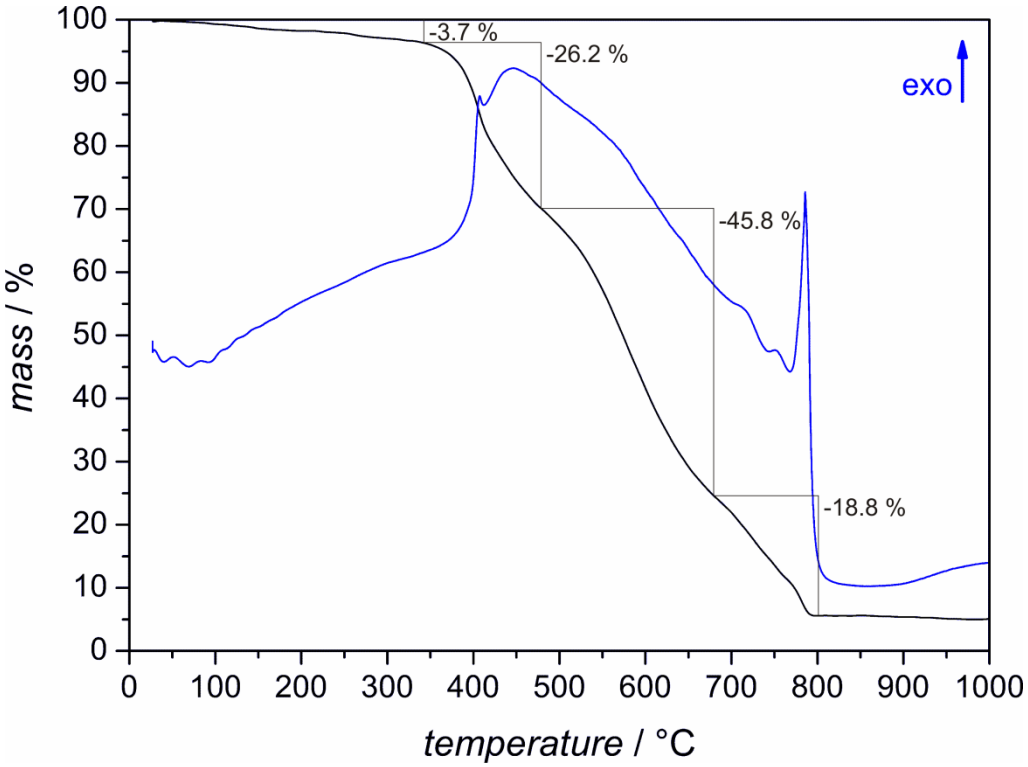


**Fig. S2** NC-**1**: TG (black) and DTA (blue) traces measured in flowing air.

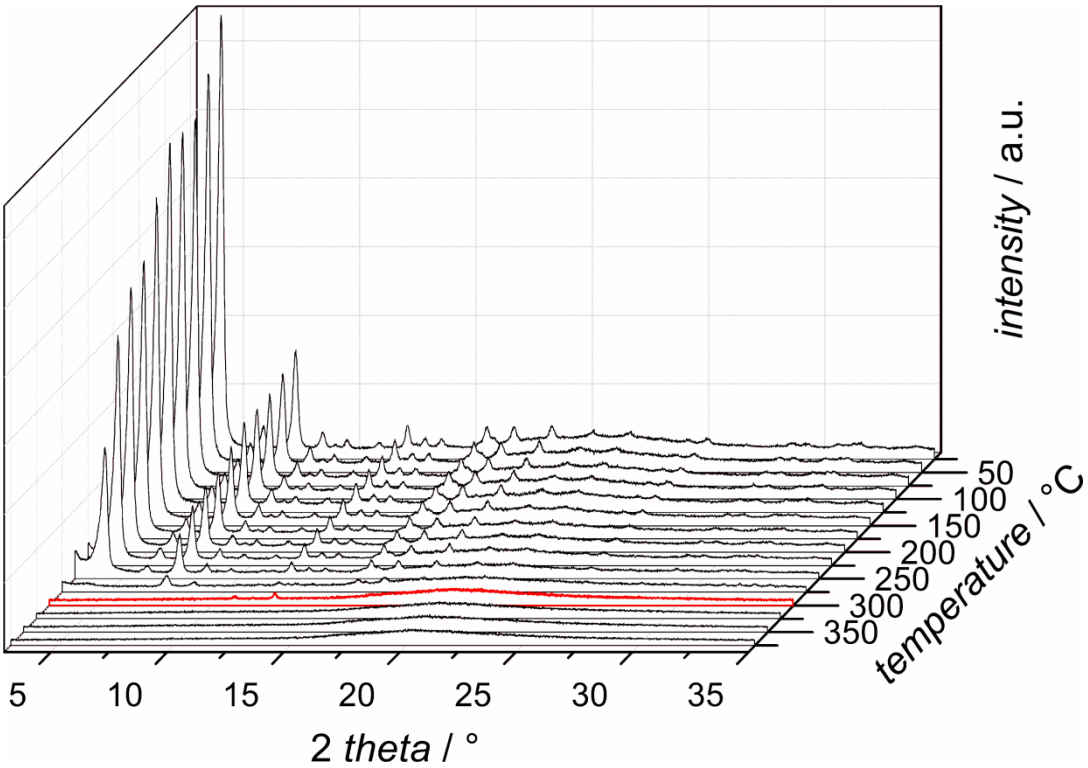


**Fig. S3** NC-**1**: VT-XRD patterns measured in air. The red pattern (300 °C) exhibits two weak reflections belonging to lcs-type **3**, at higher temperatures only amorphous material exists.

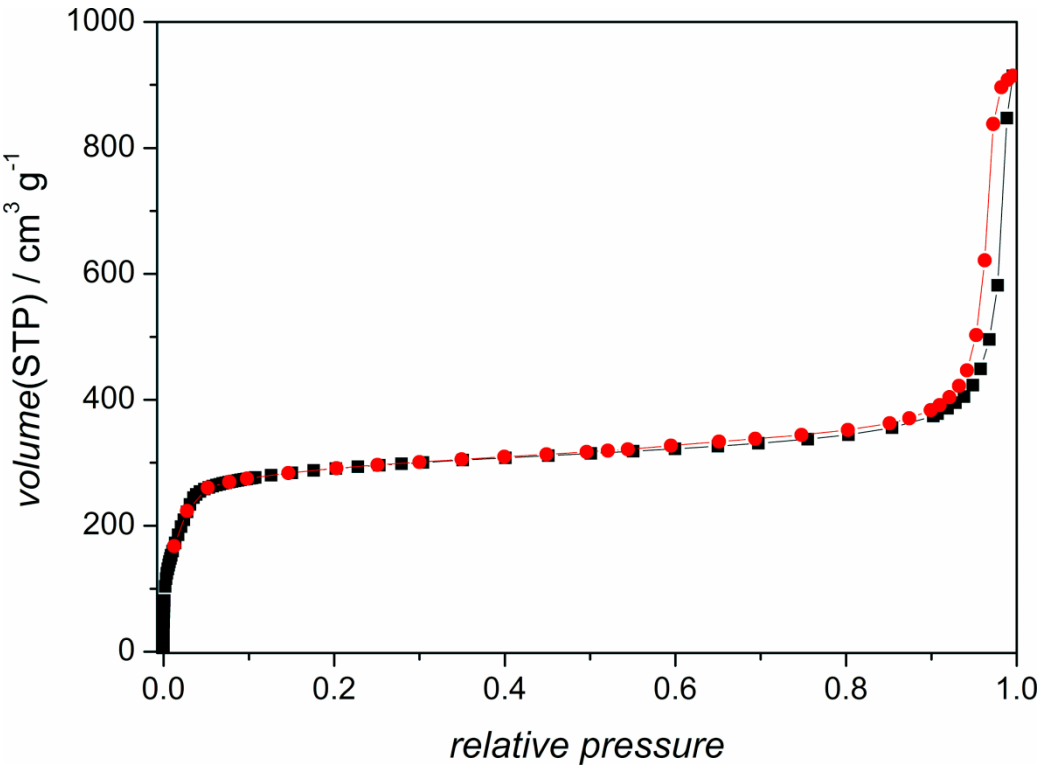


**Fig. S4** NC-**1**: Ar adsorption (black) and desorption (red) isotherms measured at –186 °C. The adsorption-desorption hysteresis loop at $p/p_0 > 0.9$ originates from inter-particle mesopores.

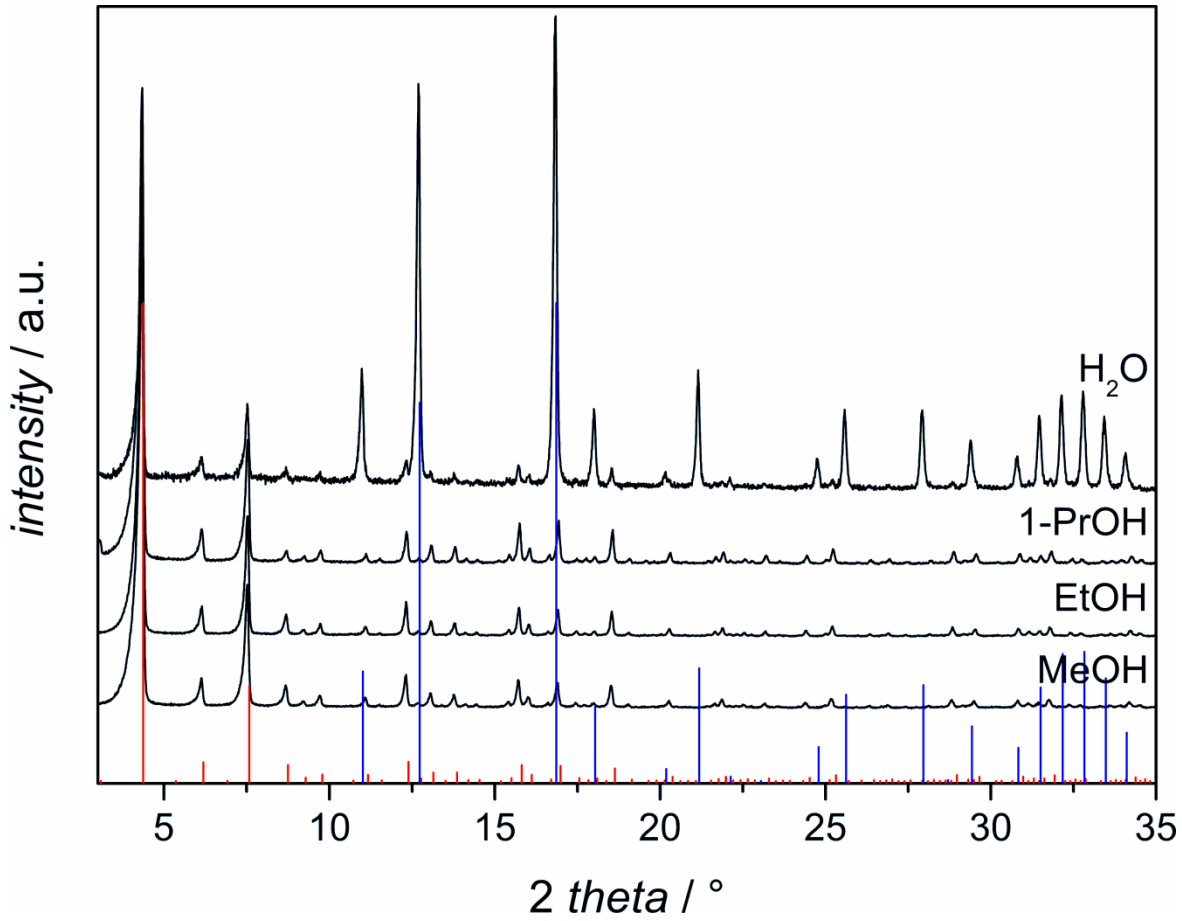


**Fig. S5** XRD patterns recorded after NC-**1** had been kept in various liquids (as indicated on the right-hand side) at room temperature for 7 d. Simulated XRD patterns of **1** (red bars) and **3** (blue bars) are presented for comparison.

## 2. Solution mediated phase transformations

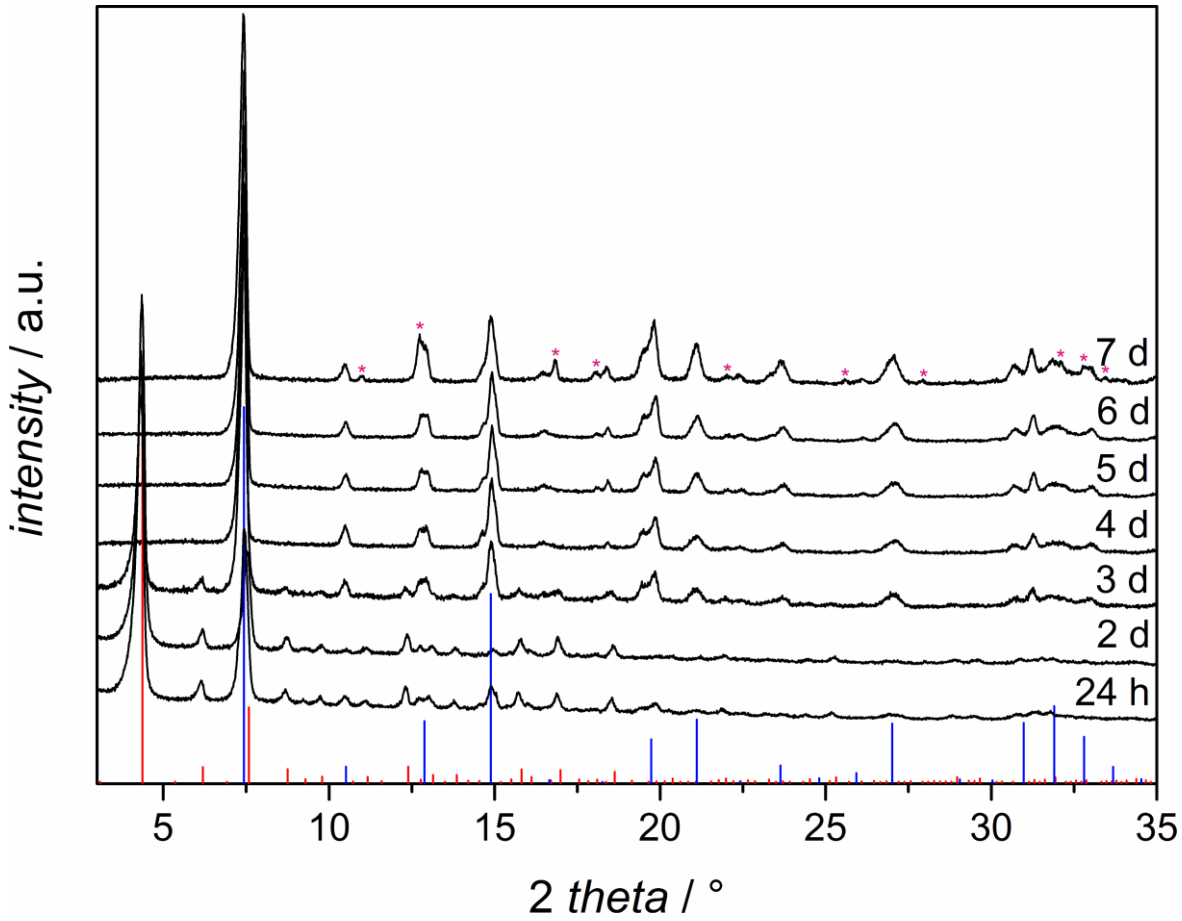


**Fig. S6** XRD patterns recorded at different time intervals (as indicated on the right-hand side) during the solution mediated transformations of NC-**1**. Simulated XRD patterns of **1** (red bars) and **2** (blue bars) are presented for comparison; the pink asterisks indicate reflections that belong to lcs-type **3**.

## 3. Synthesis of 2 *via* coordination modulation

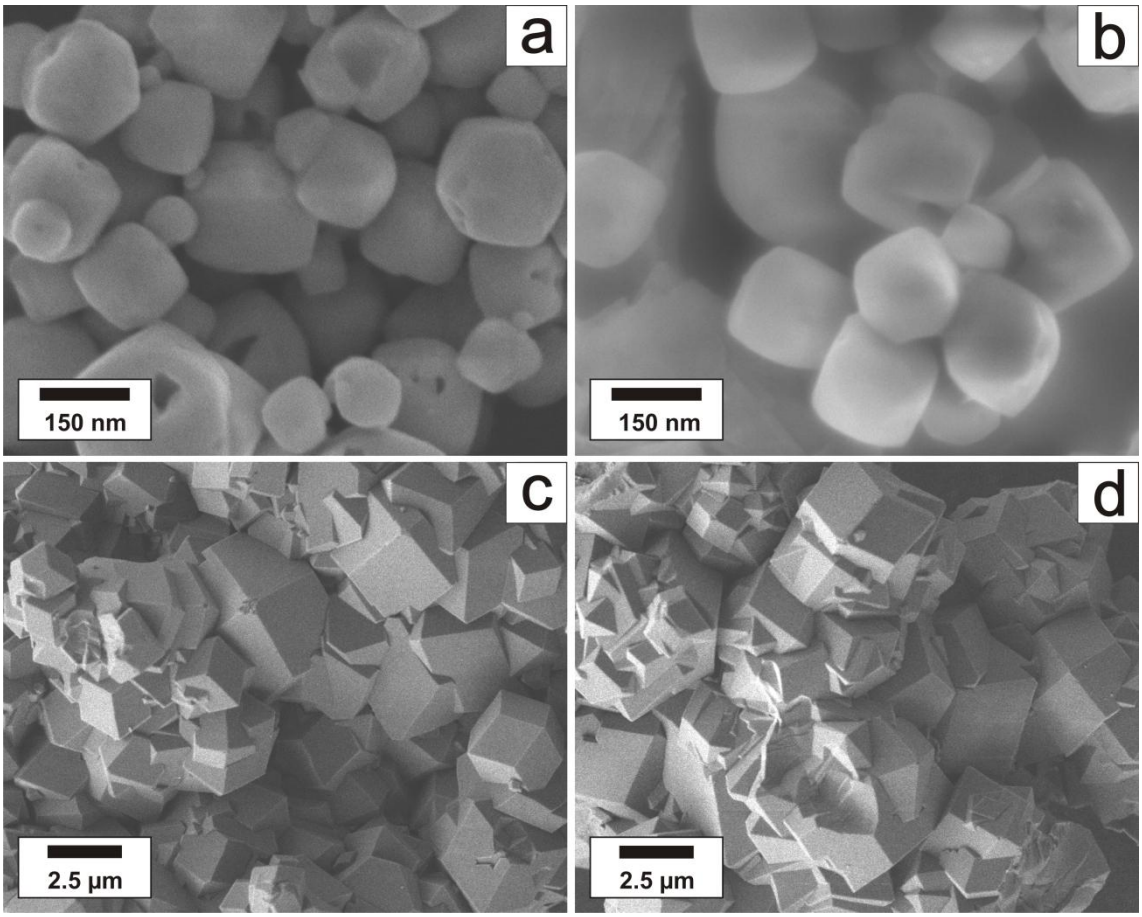


**Fig. S7** SEM images taken from products of modulated syntheses with the molar ratios Zn/Hdcim/1-mim/1-PrOH = 1 : 4 : *x* : 1000; (a) *x* = 1, *t* = 10 min; (b) *x* = 1, *t* = 24 h; (c) *x* = 3, *t* = 24 h; (d) *x* = 4, *t* = 24 h.

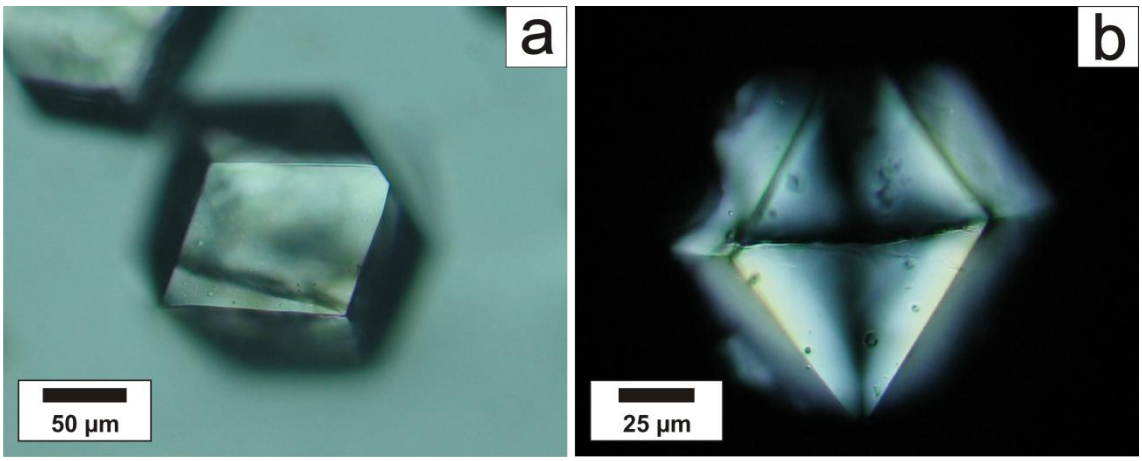


**Fig. S8** Optical images showing typical single crystals of **2** obtained by modulated syntheses at 50 °C. These crystals are birefringent and are likely twins of non-cubic domains (a), some batches consisted of crystals exhibiting Maltese crosses in addition (b).

## 4. Synthesis of 2 *via* a solvent assisted ligand exchange-related process

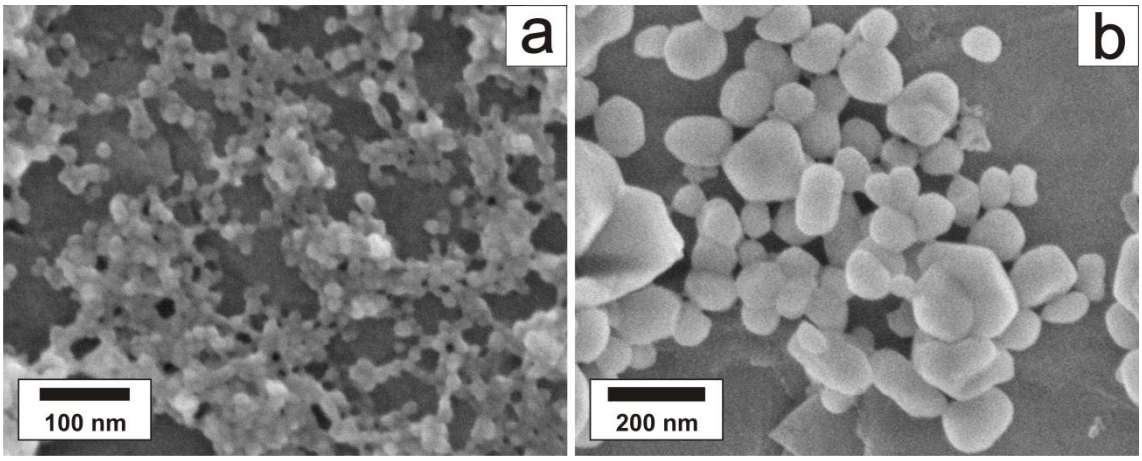


**Fig S9** SEM images of the NC-ZIF-8 template used for SALE (a) and the NC-**2** product obtained after SALE (b).

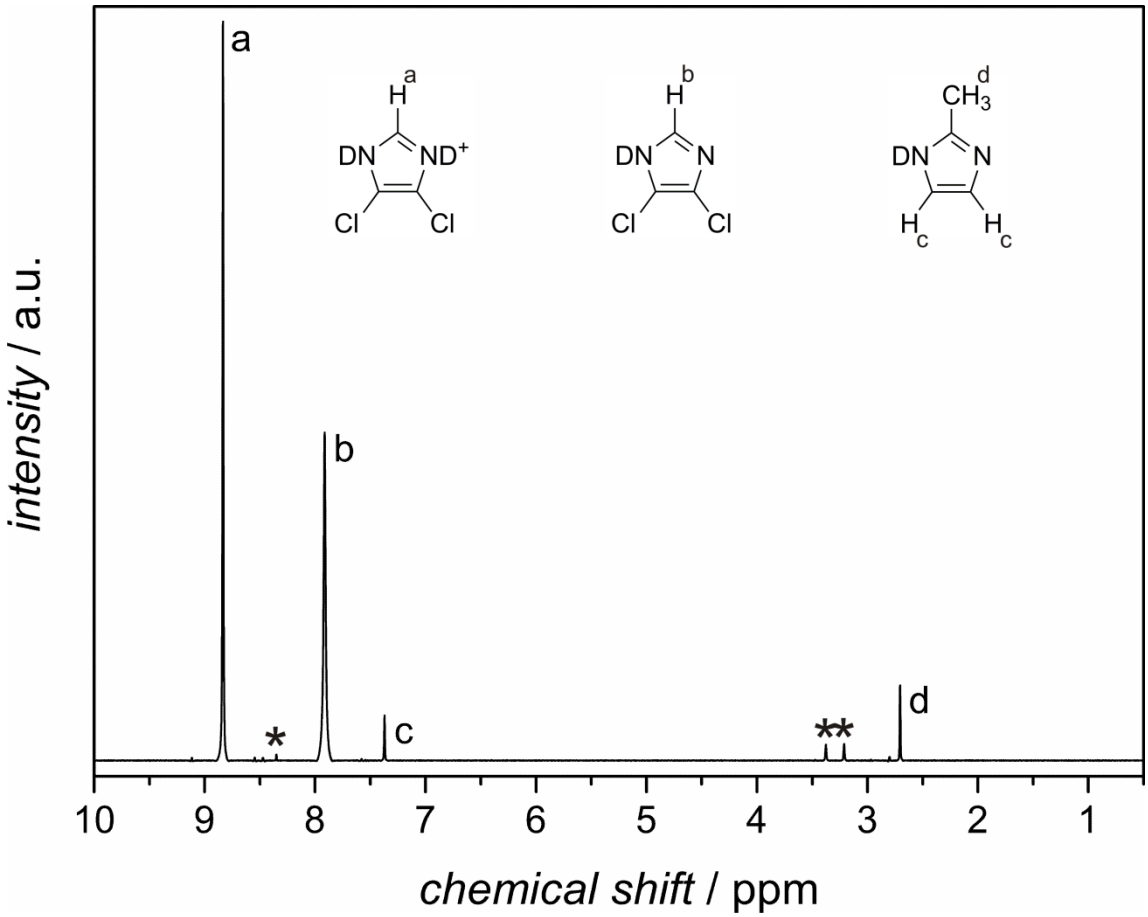


**Fig. S10** $^{1}$H-NMR spectrum of NC-**2** after digestion in a 2:1 (V/V) DCl/$D_2O$ mixture. In the acidic solution equilibria between the linkers (Hdcim and H(2-mim)) and the respective protonated forms ($H_2$dcim or $H_2$(2-mim)) exist. The degree of ligand exchange was obtained from the intensity ratio $(I_a + I_b)/(I_a + I_b + I_d)$. Impurities in the solvent are marked by asterisks.

## 5. Crystal structure analysis of 2

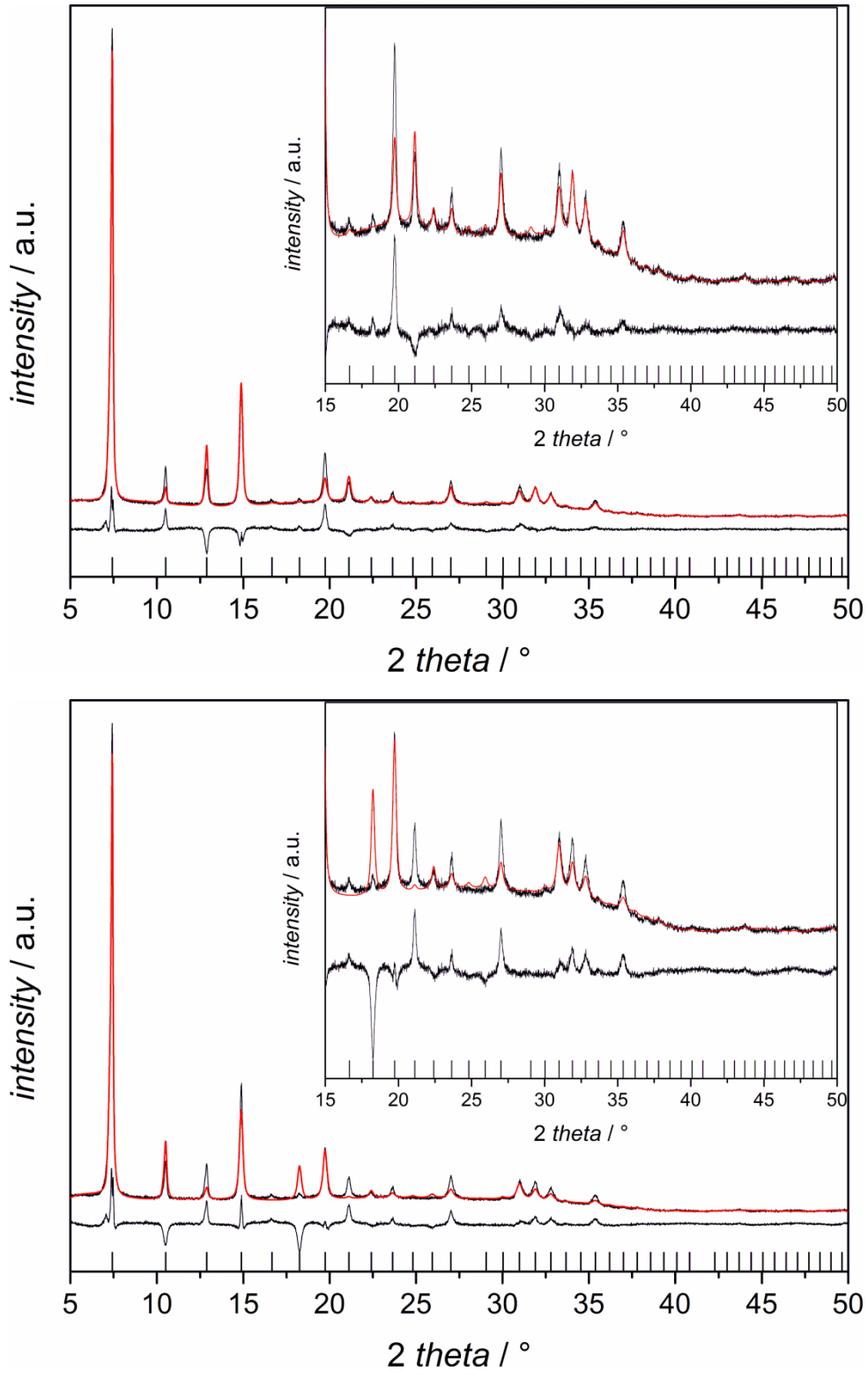


**Fig S11** Rietveld refinement plots for framework **II** (top panel) and framework **I** (bottom panel). In each panel is shown the observed (black) and calculated (red) pattern, the difference plot and the Bragg peak markers. For clarity, the insets show expanded views of the range 15-50° 2$\theta$.
Residuals (framework **II**): $R_p$ = 5.297, $R_{wp}$ = 7.979, $R_{exp}$ = 2.669, GOF = 2.989, $R_{Bragg}$ = 7.579.
Residuals (framework **I**): $R_p$ = 7.037, $R_{wp}$ = 11.336, $R_{exp}$ = 2.669, GOF = 4.247, $R_{Bragg}$ = 9.051.

**Table S1** Atomic coordinates and isotropic displacement parameters (Å$^2$) for desolvated framework **II**

| **Atom*** | **site** | ***x*** | ***y*** | ***z*** | $U_{iso}$ |
|---|---|---|---|---|---|
| Zn | 12d | 0.75 | 1.0 | 0.5 | 0.129(9) |
| N1 | 48h | 0.8082 | 0.9015 | 0.4843 | 0.128(7) |
| C2 | 24g | 0.8861 | *x* | 0.4837 | 0.128(7) |
| H2 | 24g | 0.9265 | *x* | 0.4829 | 0.128(7) |
| C4 | 48h | 0.7710 | 0.8289 | 0.4854 | 0.128(7) |
| Cl | 48h | 0.6696 | 0.8179 | 0.4865 | 0.128(7) |

*The atoms of the dcim linker (N1, C2, H2, C4, Cl) were refined as a rigid body.

**Table S2** Bond lengths (Å) for desolvated framework **II**

| | | | |
|---|---|---|---|
| Zn–N1 | 1.94124(47) | N1–C2 | 1.33609 |
| C2–H2 | 0.95992 | N1–C4 | 1.37336 |
| C4–C4#1 | 1.37662 | C4–Cl | 1.71553 |

Symmetry operation: #1 *y*,*x*,*z*

**Table S3** Bond angles (°) for desolvated framework **II**

| | | | |
|---|---|---|---|
| N1–Zn–N1#1 | 104.755(67) | N1–Zn–N1#2 | 119.38(16) |
| Zn–N1–C2 | 131.402(76) | Zn–N1–C4 | 121.801(94) |
| C2–N1–C4 | 105.954 | N1–C2–N1#3 | 112.340 |
| N1–C2–H2 | 123.830 | N1–C4–C4#3 | 107.876 |
| N1–C4–Cl | 123.269 | Cl–C4–C4#3 | 128.855 |

Symmetry operations: #1 1.5–*x*,0.5+*z*,1.5–*y*; #2 *x*,2–*y*,1–*z*; #3 *y*,*x*,*z*

## 6. Characterisation of 2

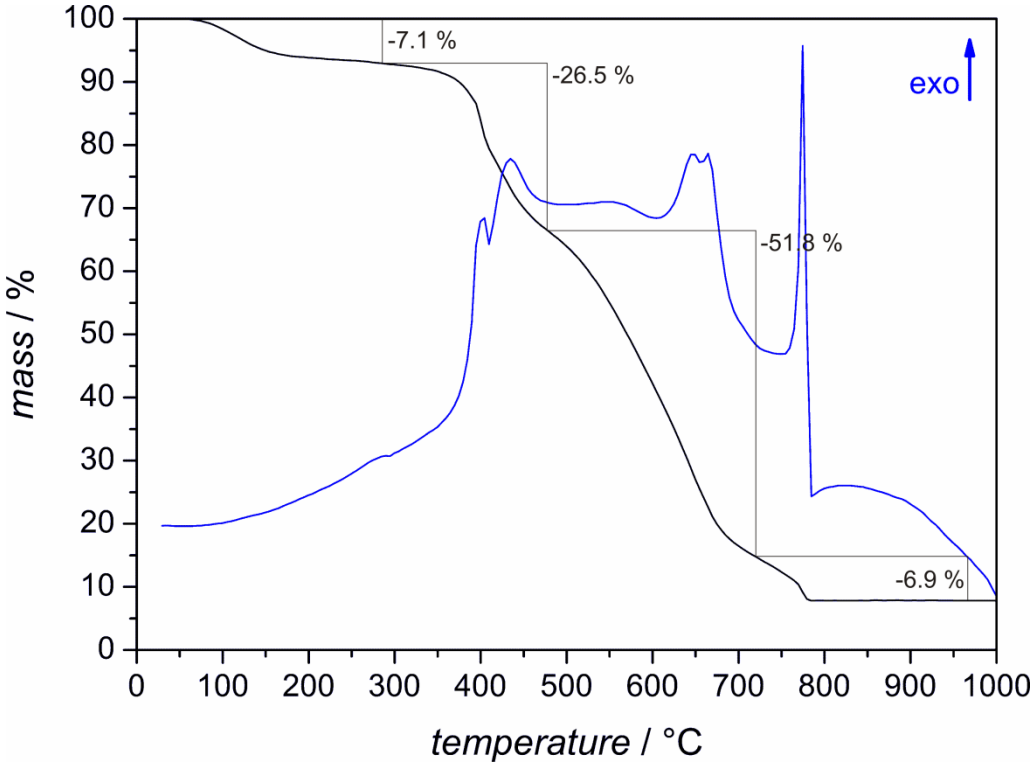


**Fig. S12** MC-**2**: TG (black) and DTA (blue) traces measured in flowing air.

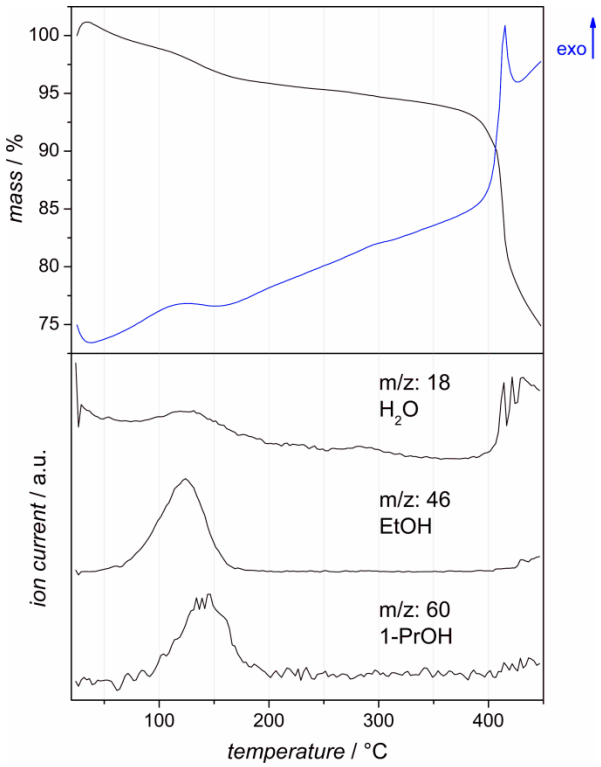


**Fig. S13** MC-**2**: TG (black) and DTA (blue) traces and simultaneously recorded mass spectrum revealing the escape of solvent species during the first mass loss up to 300 °C.

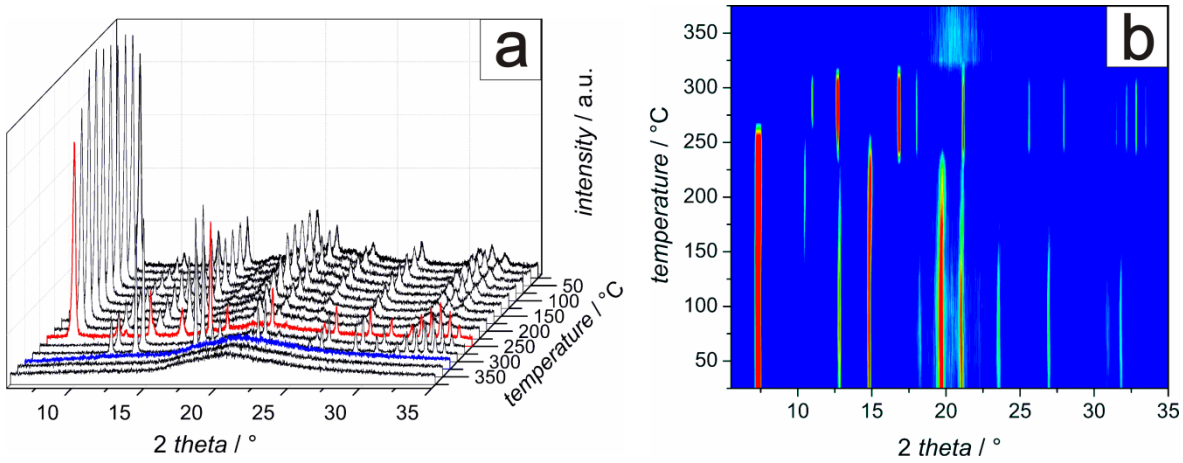


**Fig. S14** MC-**2**: VT-XRD patterns measured in air presented as stack plots (a) and contour plots (b). In (a) the red pattern (250 °C) exhibits reflections of both **2** and **3**; the blue pattern (325 °C) corresponds to amorphous material. The intensity changes upon solvent escape at ca. 150 °C are clearly seen in (b).

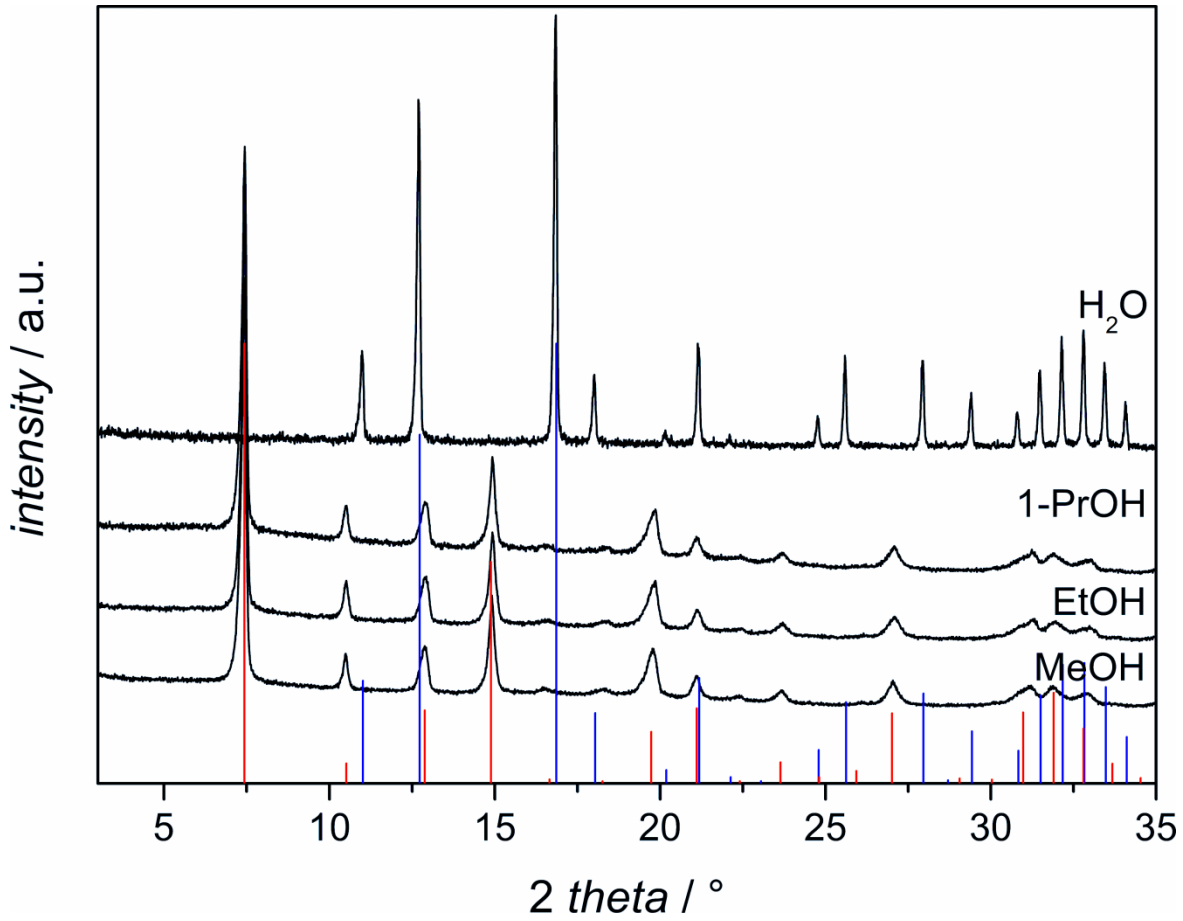


**Fig. S15** XRD patterns recorded after MC-**2** had been kept in the various liquids (as indicated on the right-hand side) at room temperature for 7 d. Simulated XRD patterns of **2** (red bars) and **3** (blue bars) are presented for comparison.